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VII.

Researches on the Volatile Hydrocarbons.

BY C. M. WARREN.

Communicated October 11*th*, 1864.

Introductory Remarks. — While engaged, a few years since, in attempting to separate some of the constituents of coal-tar naphtha by the common process of fractional distillation, I was forced to the conviction that that process could not be safely relied upon for anything like a complete and accurate analysis of such a complex mixture of liquids; and that, at best, the products thus obtained could not be regarded as anything better than remote approximations to pure substances; leaving reason to fear that there might still be other bodies present, in lesser quantities perhaps, which had escaped detection.

An examination of the results of previous researches on tars, petroleums, etc., served in general to confirm the impressions induced by my own less extended experiments; and to increase, rather than lessen, the doubts already existing in my mind as to the trustworthiness of the results which had hitherto been published concerning the neutral constituents of such mixtures. Influenced by these considerations, and by the belief that, if I could succeed in finding a process capable of effecting a more complete separation of the constituents of such mixtures, it might probably lead to the discovery of new bodies, lying between those which had already been described, — I was led to undertake the researches, the results of which I am about to record. Even if this chief purpose should fail, I was convinced that the expenditure of labor in isolating those bodies in a state of greater purity, would be amply compensated by the much needed confirmation, or perhaps correction, of the results previously published, in addition to the valuable incidental evidence of the absence of other bodies which would thus be furnished. The results which I have obtained in the pursuit of this object are abundantly sufficient to show that I did not undervalue the work of my predecessors, nor over-estimate the importance of the work before me.

The success which attended my efforts in search of a better process of separation has already been described in detail, in a memoir "On Fractional Condensation," etc. (Memoirs of the American Academy, 1864.)

This new process was first applied, more especially for the purpose of testing its efficiency, in the separation of benzole from coal-tar naphtha. This mixture was selected for the test on account of the property which benzole possesses, in contradistinction from its associates, of being crystallizable at a low temperature, thus affording an additional test of the purity of the product which might be obtained by the process of fractioning. Somewhat to my surprise I found that, after only the fifth series of fractionings, I had obtained benzole so nearly pure that the whole of it would distil from a tubulated retort between 80° and 81° C.; and that when congealed, which was effected by placing the containing bottle in pounded ice, not a drop of liquid could be poured from the mass of crystals. From this result, — which, at the least, indicated a near approximation to purity, — taken in connection with other favorable indications, I felt confident that I had accomplished my first object, and had found a process that could, in all probability, be successfully applied in the study of the petroleums, which up to that time (1861) had baffled every attempt to resolve them into their proximate constituents.

Being naturally anxious to apply the new process in this seemingly more promising field of inquiry, I at once suspended, for the time being, my operations on coal-tar naphtha, and commenced simultaneously the investigation of Pennsylvanian petroleum, and of the oils distilled from Albert coal (from Hillsboro, New Brunswick) in the process of manufacturing illuminating oil. These two substances, neither of which had ever been made the subject of special scientific investigation, were selected as being fair representative types, on the one hand of the native liquid petroleums, and on the other of the artificial coal oils. The comparative study of these two substances seemed to promise additional interest on account of the close analogies which they present, especially when this circumstance is considered in connection with the fact of their great diversity of origin. This is the limit which at that time was assigned for these researches; my intention being, so soon as the separations and analyses should be completed, and the boiling-points and some of the other more important physical characteristics determined, briefly to publish the results, together with the process of fractioning, — preliminary to a complete memoir at a more advanced stage of the work. Before this work had been accomplished, however, it became evident that the bodies contained in these mixtures could not be studied so satisfactorily by themselves as in comparison with other series of hydrocarbons, especially with reference to certain important questions of more general interest; for example, the question in regard to the increment of boiling-point corresponding to the addition of $C_2 H_2$ in homologous series. It was therefore deemed advisable to extend the inquiry so as to include the naphthas from coal- and wood-tars, and the oil of cumin. And there are still other mixtures of hydrocarbons, that have been made the subjects of previous research, which must yet be brought into the work, in order to clear up, in a satisfactory manner, the confusion and obscurity that seem to exist in our publications regarding some questions relating to the different series of this class of bodies.

This digression from my original plan, having caused much additional labor, has necessarily delayed publication longer than was desirable, until now the results of more than three years of work have accumulated. In this connection I may remark, so far as regards petroleum, that I had nearly completed the fractional separations — except of the bodies of high boiling-point — so long ago as June, 1862, having been for a long time occupied with this work before the appearance, in that month, of the first memoir of Pelouze and Cahours on the same subject. At that time my work was considerably in advance of theirs, and their results differed widely from mine in some important particulars; yet after the publication of their memoir I felt reconciled to a continuance of the delay which had been caused by the change of plan above mentioned, considering it due to these chemists that they should have time to complete the publication of the results of their investigations before I should publish mine. Similar remarks might be made respecting the first publication of Schorlemmer, which appeared soon after, on the products of distillation of cannel coal; this substance being so closely analogous to the Albert coal (upon the products of which I had at that time been long engaged) as to induce the belief that, under the same circumstances, either would afford the same products.

I.

On the Volatile Hydrocarbons from Coal-tar Naphtha, Oil of Cumin, and Cuminic Acid.

PART I.

HYDROCARBONS FROM COAL-TAR NAPHTHA.

In presenting the results of a re-examination of a series of substances upon which so much labor had already been bestowed, and upon the nature and properties of which so little doubt has seemed to exist, it may confer an interest on the subject to state briefly some of the more important results and conclusions that previous investigators have arrived at in the study of these substances.

The discovery by Faraday,* in 1825, of benzole ("bicarburetted hydrogen") in the oil compressed from oil-gas, rendered it highly probable, and indeed led this distinguished philosopher to suspect, that this substance might be found in coal-tar naphtha. His search for it, however, proved unsuccessful, it having been first detected by Hofmann in 1845.† This chemist, however, did not attempt to isolate this body, and the bare fact of its presence appears to be all that was definitely known of the composition of coal-tar naphtha prior to 1849, in which year Mansfield ‡ published his elaborate and valuable research, being the first effort at a proximate analysis of this mixture which appears to have been attended with any considerable measure of success. Although a fatal accident, while engaged in his experiments, prevented Mansfield from completing the investigation which he had so well begun, yet the work that he had already published in an unfinished state must always be regarded as having contributed much towards a clear and definite knowledge of the nature of the neutral pyrogenous oils contained in coal-tar naphtha. Indeed, it may be said that little has since been added to our knowledge on this subject. Notwithstanding the incompleteness of his separations of the hydrocarbons, the extent to which he had carried them, with the limited means employed, is truly remarkable, and could not have been accomplished without an expenditure of labor, and a degree of patient endurance, which only those who have experienced the tediousness of such operations can appreciate.

Mansfield claimed to show that the light coal-tar naphtha is composed of a mixture of four distinct hydrocarbons, boiling within the range of 80° to 175°, C.; and probably having the general formula $C_n H_{n-6}$. The first of these, which he found to boil constant at 80°, was proved to be identical with benzole, $C_{12} H_6$. The second, boiling at about 113°, was determined, from certain reactions, to be identical with toluole, $C_{14} H_8$. The special study of this body was deferred, however, with the remark that it had not yet been isolated in a state of sufficient purity to claim an analysis. The third body, boiling at about 140° to 145°, was said to present all the characteristics of cumole, $C_{18} H_{12}$; but this view was not founded on a careful study and comparison of the chemical or physical properties of these bodies, but was merely an expression of opinion in advance of anticipated results. Of the fourth body, boiling at about 170° to 175°, Mansfield remarks that it bears so strong a resemblance, in odor and other properties, to cymole, $C_{20} H_{14}$, as to induce the belief that this substance is identical with the hydrocarbon existing in oil of cumin. It thus appears that of the four bodies which Mansfield detected in coal-tar naphtha, benzole is the only one which he had studied in any detail. Indeed he distinctly states that the others had not yet been isolated in such a state of purity as to entitle them to analysis. And yet his conjectures as to the identity of these bodies, thrown out by way of preliminary notice of results which were acknowledged to be incomplete and inaccurate, have nevertheless been extensively quoted, and generally received as established facts. In addition to the bodies already mentioned, Mansfield also detected the presence of a body more volatile than benzole, having an alliaceous odor, which he found to boil between 60° and 70°. Ritthausen* made a re-examination of the light coal-tar naphtha, in order to obtain the hydrocarbons in a state of greater purity, and to prove the correctness of Mansfield's view of the composition of this naphtha. In regard to the results which he obtained, he says they fully confirm those of Mansfield. Of the body which Mansfield designated as probably identical with cymole, and of the oil more volatile than benzole, Ritthausen obtained quantities too small to admit of investigation. In regard to the latter, however, he remarks,† that to Mansfield's account he can add, that "its nitro-product quite resembles that of benzole, and hence that at all events it belongs to the series $C_n H_{n-6}$, and perhaps has the formula $C_{10} H_4$."‡ It is to be regretted that Ritthausen also omitted to analyze and determine the vapor density of any one of these substances, he having added, therefore, nothing more than a confirmation of the results of Mansfield. He gives the boiling-point of benzole at 80°, of toluole at 109°, and of the so-called cumole at 139 – 140°, which will be found to agree very nearly with my own determinations. Church,§ in the following year, published a paper on the "Determination of Boiling-points" in the "Benzole Series." I cannot better present his results than by quoting the following table: —

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* Philosophical Transactions of the Royal Society, 1825, CXV. 465.

† Annalen der Chemie und Pharmacie, 1845, LV. 200.

‡ Quarterly Journal of the Chemical Society, 1849, I. 244.

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* Journal für praktische Chemie, 1854, LXI. 74.

† "Ich kann den Angaben von Mansfield über das letztere nur das hinzufügen, das seine Nitroproducte denen des Benzols, etc. ganz ähnlich sind, daher es jedenfalls der Reihe $C_n H_{n-6}$ angehört und vielleicht die Formel $C_{10} H_4$ besitzt."

‡ On a future occasion I shall show that Ritthausen was in error in placing this body in the benzole series, and indeed in considering it as a hydrocarbon at all. He was evidently deceived by operating on a mixture containing benzole. Furthermore, as Mansfield suggested might be possible, that part of the naphtha more volatile than benzole is by no means composed of a single substance. Having had a large quantity of this volatile material at my command, I have been able to obtain the separate constituents apparently in a state of great purity. Of the two bodies separated, one of them boils constant at about 40°, and the other near 0°. Both are compounds containing sulphur, and therefore will more properly form the subject of a separate paper.

§ Philosophical Magazine, 1855, 4th Series, IX. 256.

	Formula.	Boiling-point.	Difference.
Benzole,	$C_{12} H_6 = C_6 3 (C_2 H_2)$	80°.8	22°.9
Toluole,	$C_{14} H_8 = C_6 4 (C_2 H_2)$	103°.7	22°.5
Xylole,	$C_{16} H_{10} = C_6 5 (C_2 H_2)$	126°.2	22°.2
Cumole,	$C_{18} H_{12} = C_6 6 (C_2 H_2)$	148°.4	22°.3
Cymole,	$C_{20} H_{14} = C_6 7 (C_2 H_2)$	170°.7	

Church states that he obtained all of these bodies from coal-naphtha, and also that he obtained benzole from benzoic acid, toluole from toluylic acid, xylole from wood-spirit, cumole from cuminic acid, and cymole from oil of cumin; and that he has found the corresponding bodies from these different sources to be identical. It will be observed that Church claims to have found in coal-tar a body boiling at 126°.2, which he calls *xylole*, thus supplying from this source a fifth member of the benzole series; whereas Mansfield and Ritthausen found only four bodies within the range of temperature indicated by the table. It will also be observed that his determination of the boiling-point of toluole is much lower, and that of cumole much higher, than the corresponding determinations of Mansfield and Ritthausen; thus giving room for a middle member between them, and preserving a remarkable uniformity of difference — viz. 22° and a fraction — between the boiling-points of any two contiguous members of the series, for the addition of $C_2 H_2$.

That the earlier investigators had found in coal-tar naphtha only the two lower members ($C_{12} H_6$ and $C_{14} H_8$) and the two upper members ($C_{18} H_{12}$ and $C_{20} H_{14}$), indicating the absence of the middle member ($C_{16} H_{10}$) of the benzole series, was always to me an anomaly which I could not reconcile with any plausible theory in regard to the formation of these bodies; and I was led, therefore, to question whether this body had not been overlooked in making the separations. The alleged discovery of this body in coal-naphtha by Church, together with the beautiful uniformity of the boiling-point difference throughout the series which he presented, and the apparent care with which the whole research had been conducted, led me to regard his results as being more reliable than those which had previously been published. I remained under this conviction until I had discovered the boiling-point difference of 30° in other series of hydrocarbons,* which led me to doubt the accuracy of Church's determinations of boiling-points, and to consider those of Mansfield and Ritthausen as probably more correct.

In the first paragraph of his paper, Church remarks that, "although doubts still remain as to the relations of these bodies to one another, yet their composition has been ascertained with certainty." It does not appear, however, that an analysis or vapor density of any one of the members of this series, as obtained from coal-tar, except benzole, had ever been published. As already indicated by the title of his paper, it appears to have been the design of Church to treat only of the boiling-points of these bodies; yet finding that his preparations of toluole — prepared both from coal-naphtha and toluylic acid — gave a boiling-point differing considerably from observations previously published, he took occasion to make analyses of his preparations of this substance, which he regards as "perfectly satisfactory"; and adds that "the details and numerical results of these analyses, and of many others which the present inquiry necessitated, the limits and special object of the present paper do not admit of my giving here." As he undertook to correct the work of his predecessors, to do which fairly would seem to require the publication of these "details and numerical results," their omission is to be regretted, the more since he found space and purpose for matter apparently less relevant to his special subject. I am prompted to these remarks from having been led to undertake the tedious task of making a re-examination of coal-tar naphtha mainly on account of the disagreement between Church's determinations, which I have found to be mostly incorrect, and those which had been previously published.

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* See the following Memoir on this subject.

In addition to the bodies mentioned in the foregoing table, Church alludes to the discovery of two other bodies, boiling respectively at 97° and 112°. Subsequently, in a "Note on Parabenzole, a new Hydrocarbon from Coal-Naphtha,"* he publishes the details of an investigation of the former of these two bodies, which he finally found to boil "*perfectly constant at* 97°.5," and to be isomeric with benzole.

I think I shall be able to show in the following pages, —

1. That coal-tar naphtha contains only four hydrocarbons within the range of 80° to 170°, as taught by Mansfield, and confirmed by Ritthausen.

2. That the benzole series within that range of temperature is limited to four members, and therefore does not contain five, as has been generally supposed.

3. That these four members have the boiling-points 80°, 110°, 140°, and 170° respectively; and consequently that the boiling-point difference in this series, for an elementary difference of C_2H_2, is 30°, instead of 22° and a fraction, as alleged by Church.

4. That the body obtained from coal-tar naphtha, boiling at 140°, is not identical with cumole from cuminic acid, as assumed by Mansfield, nor even isomeric with it;

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* Philosophical Magazine, 1857, 4th Series, XIII. 415.

but that it has the formula which has been assigned to xylole, containing C_2H_2 less than that of cumole.

5. That the body obtained from coal-tar naphtha, boiling at 170°, is quite a different body from cymole obtained from oil of cumin, — with which it has been considered identical, as assumed by Mansfield, — these bodies differing from each other by C_2H_2.

6. That cumole from cuminic acid, and cymole from oil of cumin, do not even belong to the benzole series.

7. That the Parabenzole of Church was in all probability only a mixture of benzole and toluole.

Of the Quality of Naphtha employed in this Investigation. — As I have taken occasion to question the existence in coal-tar naphtha of two of the substances which it has been said to contain, — viz. cymole, $C_{20}H_{14}$, and parabenzole, $C_{12}H_6$, — it is a matter of some importance that I should clearly state the kind or quality of the naphtha employed. The tar from which this naphtha was obtained was a mixture of the tar furnished by the following companies, viz. the New York and the Manhattan Gas-Light Companies, of New York; Brooklyn Gas-Light Company, of Brooklyn, N. Y.; Albany Gas-Light Company, of Albany, N. Y.; and the Gas-Light Companies of Newark and Jersey City, in New Jersey. It was mostly made from Cannel and Newcastle caking coals, which were imported from Liverpool, and mixed in the proportions of one third to five eighths Cannel, to two thirds to three eighths Newcastle. In some of the works a portion of the caking coal was from mines in Pennsylvania. The tar from these different gas-works, as regularly received at the naphtha manufactory, was poured into a large tank provided for this purpose. The stills were uniformly charged with tar directly from this tank; so that there can be no doubt that the naphtha employed was made from a mixture of the tar supplied by the six different companies above enumerated. Most of the gas-works referred to are large, the annual production of tar amounting in the aggregate to upwards of 50,000 barrels. It does not appear, therefore, that the absence of the bodies in question from the naphtha which I have employed, can be attributed to any peculiarity of the tar. The naphtha was prepared in a manufactory in New York over which I had at that time personal control, and was purified under my own direction. The process of purification did not differ essentially from that in common use in England, the reagents employed being oil of vitriol and alkali. One hundred barrels of the purified naphtha were subjected, under my personal superintendence, to repeated fractional distillation from an iron still. The chief object in operating on so large a quantity, was to insure the detection of any constituent which might be present in small proportion. The process of fractioning was continued on this large scale until the separations had so far progressed, that at certain temperatures a full barrel of distillate would come off from the ten-barrel still employed, without a variation of more than one or two degrees of the thermometer. Finally a sample gallon was taken from each of the barrels composing the last series of products, and these samples were set aside for this investigation, which was afterwards conducted in the laboratory.

Of the Results of Fractional Condensation. — Such of the samples above mentioned as promised to yield the different constituents of the naphtha in the largest proportion, were subjected to repeated series of fractionings by my process of "Fractional Condensation."[*] As full details of this process have already been given in the memoir referred to, it will be needless to repeat them here. It will suffice to say that the fractioning in this case was conducted in all respects as there described, and continued until the whole of the naphtha taken, boiling between 80° and 170°, had accumulated at the four points already indicated, viz. at 80°, 110°, 140°, and 170°; or so nearly the whole that the intermediate quantities had become too small to admit of being further operated upon. Having therefore so thoroughly exhausted the intermediate fractions, I can have no hesitation in asserting that no other body than those alluded to was present in the naphtha, — at least, in appreciable quantity, — hence, that the parabenzole of Church was probably only a mixture of benzole and toluole. I may here remark that each of the sample-gallons employed, when subjected to my process of fractioning, was found to contain, in variable proportion, all of the constituents of the naphtha.

Of some of the Properties of the Bodies obtained by Fractioning.

1. BENZOLE.

Specific gravity, 0.8957 at 0°, and 0.882 at 15°.5.[†]

Determination of Boiling-point. — This experiment was conducted in a tubulated retort, operating on 150–200 *c. c.* of the benzole, containing some pieces of sodium. The benzole employed had previously been repeatedly boiled with sodium, until the latter ceased to have any action. The thermometer bulb extended into the liquid * nearly to the bottom of the retort. A second thermometer was attached, by means of flexible bands, to the side of the one in the retort; the bulb being placed, during ebullition, at a point midway between the centre of the cork (— 5°) and the upper end of the mercurial column, viz. at 35°. A paper screen, closely fitting the thermometer spindle, was placed across at the top of the cork. With the retort neck slightly inclined upward, and cooled to prevent the escape of vapor, ebullition was continued for considerable time, until the mercury in the thermometer ceased to rise. The lamp being removed for the moment, the neck of the retort was then turned downward, and quickly inserted in a Liebig's condenser. On replacing the lamp, distillation commenced almost immediately at 79°.

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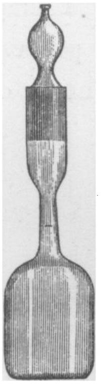
[*] Memoirs of the American Academy, 1864.

[†] It would appear that the specific gravities of liquids are usually determined at the temperature of the air. The result of this is that the determinations made by different observers are not comparable with one another. That these specific gravities are not uniformly taken at 0° C. — the temperature which, on account of greater convenience, etc. is generally acknowledged to be preferable — is probably due to the fact that the more

Observations. —

Temperature. °		Time. h. m.		Temper. by Side Thermom.
79.0	at	2.40	5 minutes.	
79.2	"	2.45	15 "	22°.
79.4	"	3.00	12 "	24°.
79,5	"	3.12	20 "	25°.
79.6	"	3.32	18 "	26°.
79.6	"	3.50		26°.

common specific gravity bottle is not suited to this purpose. Indeed, with a volatile body that bottle cannot serve for an accurate determination at any temperature. A reform in this regard being highly desirable, I would call attention to a specific gravity bottle which I obtained a few years ago from Fastrè, in Paris, which is admirably adapted for taking specific gravities, even of volatile liquids, at a low temperature. The accompanying figure represents this bottle of one half its natural size. Who was the author of this particular form I am not informed, although it may have been already noticed in some publication. A bottle analogous to this is figured by Schiel ("Einleitung in das Studium der organischen Chemie," page 76); but his bottle has an oval bottom, which makes it less convenient. The particular advantage of this bottle over the more common one, which advantage Schiel omits to notice, consists in this: that the space or chamber above the line on the capillary neck is large enough to allow for the expansion of the liquid consequent upon the elevation of temperature from 0° to that of the surrounding air; and that the ground stopper fits so closely that no perceptible loss from evaporation can take place during the time occupied by an experiment.



In order to furnish determinations of the specific gravities of the bodies to be treated of in these researches, which shall be comparable with corresponding determinations by other observers, I shall generally record one or more special determinations made for this purpose.

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* For critical remarks on the question of propriety of placing the thermometer bulb in the liquid, etc.; and for further details of the method of taking boiling-points, especially at low temperatures, see the accompanying Memoir, "On the Influence of C_2H_2 on the Boiling-points in Homologous Series of Hydrocarbons," etc.

Distillation therefore occupied one hour and ten minutes, during which time the thermometer rose only 0°.6, being fifty minutes in rising 0°.2 from 79°.4 to 79°.6, at which temperature it had distilled nearly to dryness. Height of the barometer during the experiment reduced to 0° = 761.9mm. Taking 79°.4, this being the average of the last five observations, and applying the corrections for the upper column of mercury, and for atmospheric pressure, according to the directions given by Kopp,* we find the corrected boiling-point of benzole to be 80°.1.

Analysis. — 0.2339 gramme of benzole gave, by my process† of combustion in a stream of oxygen gas, 0.7903 of carbonic acid, and 0.1683 of water.

		Calculated.		Found.
Carbon,	C_{12}	72	92.31	92.15
Hydrogen,	H_6	6	7.69	7.99
		78	100.00	100.14

Determination of Vapor Density. —

Temperature of balance,	15°
Temperature of oil bath,	171°
Height of barometer,	764.1mm. at 9°
Increment of balloon,	0.2447
Capacity of balloon,	265 *c. c.*

Density of vapor found,	2.688
Theory $C_{12}H_6$ = 4 volumes,	2.698

2. TOLUOLE.

Specific gravity, 0.8824 at 0°, and 0.872 at 15°.

Determination of Boiling-point. — The preparation employed for this determination had also been repeatedly boiled with sodium until the latter ceased to have any action upon it. Operating in this case also upon a pretty large quantity, the distillation occupied about an hour. The experiment was conducted as detailed under the head of Benzole. Distillation commenced at 110°.6; two minutes later the temperature had fallen to 110.4, at which point it remained absolutely constant during the lapse of forty-eight minutes. Five minutes later the temperature had risen again to 110°.6;

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* Poggendorff's Annalen, 1847, LXXII. 38.

† Proceedings of the American Academy, 1864, p. 251.

and five minutes later to 110°.8, at which point, having distilled nearly to dryness, the operation was suspended. The corrections for pressure (— 0°.16) and for the upper column of mercury — which, with the thermometer used in this experiment, was only 7° in length, — gives 110°.3 as the corrected boiling-point of toluole. Church* remarks that toluole, when distilled in the ordinary manner, is liable to become oxidized, and its boiling-point thereby raised, in consequence of the upper part of the retort becoming heated above the boiling-point of toluole. He found that toluole which, by ordinary distillation, had come over between 108° and 109°, would distil eight tenths between 103° and 104°, after repeated purification with sodium. I would therefore state that my preparation of toluole was never subjected to a temperature above its boiling-point; and that I have never noticed any reduction of the boiling-point of this body by purification with sodium.

Analysis. — 0.1628 gramme of toluole gave, by combustion in a stream of oxygen gas, 0.5447 of carbonic acid, and 0.1315 of water.

		Calculated.		Found.
Carbon,	C_{14}	84	91.3	91.20
Hydrogen,	H_8	8	8.7	8.97
		92	100.0	100.17

Determination of Vapor Density. —

Temperature of balance,	17°
Temperature of oil bath,	209°
Height of barometer,	760.1$^{mm.}$ at 15°
Increment of balloon,	0.287
Capacity of balloon,	249.5 *c. c.*

Density of vapor found,	3.2196
Theory $C_{14} H_8$ = 4 volumes,	3.1822

3. XYLOLE. (*Cumole of Mansfield and Ritthausen.*)

Specific gravity, 0.878 at 0°, and 0.866 at 15°.5.

Determination of Boiling-point. — This determination was made in all respects like that of benzole, the xylole employed having been also subjected to the same treatment. The quantity operated upon was, however, smaller, and the experiment conducted more rapidly. Distillation began at 138°.6, and terminated at 139°, having distilled almost to dryness. The time occupied was seventeen minutes. Taking the average of these observations, viz. 138°.4, and applying the customary corrections, we find 139°.8 to be the corrected boiling-point of xylole.

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* Philosophical Magazine, 1855 (4), IX. 256.

Analysis. — 0.1333 gramme of xylole gave, by combustion in a stream of oxygen gas, 0.4413 of carbonic acid, and 0.1185 of water.

		Calculated.		Found.
Carbon,	C_{16}	96	90.57	90.29
Hydrogen,	H_{10}	10	9.43	9.87
		106	100.00	100.16

Determination of Vapor Density. —

Temperature of balance, ...	16°.5
Temperature of oil bath, ...	207°.5
Height of barometer, ...	$760^{mm.}$ at 14°
Increment of balloon, ...	0.3528
Capacity of balloon, ...	228 *c. c.*
Density of vapor found, ...	3.7517
Theory $C_{16}H_{10}$, ...	3.6665

These results show clearly that this body has the formula $C_{16}H_{10}$, and that it is doubtless the third member of the benzole series.* Although xylole, first discovered by Cahours in the oil separated from wood-spirit, has had a much lower boiling-point assigned to it, I have retained that name for this body, since the results which I have obtained in the study of the light oil from wood-tar indicate that when the corresponding body from this source is in a state of equal purity, its boiling-point will agree with the above determination. I may here mention that in my researches on the light oil from wood-tar, I have obtained a body at about 140°, but nothing between that and 110° (these temperatures are not corrected), although special pains were taken to work up the intermediate fractions. So that I am in a position to justify the assertion that no other body was present in appreciable quantity between the temperatures mentioned.

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* As this memoir is passing through the press, the receipt of my journals for September calls attention to late publications of Hugo Müller, Béchamp, and Naquet concerning this hydrocarbon. Müller concludes that it is xylole, a result which agrees with my own. (Annalen der Chemie und Pharmacie, 1864, CXXXI. 321.) Béchamp, on the contrary, erroneously regards it as being a *new* hydrocarbon, not belonging to the benzole series. (Bulletin de la Société Chimique, Paris, 1864, 204.) Naquet also calls it a *new* hydrocarbon, and gives it the formula $C_{18}H_{12}$. (Bulletin de la Société Chimique, Paris, 1864, 205.)

That this body from coal-tar naphtha, boiling at 140°, is not identical with cumole from cuminic acid, will be made apparent on comparison of the results above stated, with those which will be given when treating of cumole.

4. ISOCUMOLE. (*Cymole of Mansfield.*)

Specific gravity, 0.8643 at 0°, and 0.853 at 15°.

Determination of Boiling-point. — This was conducted with the usual precautions, and under conditions similar to those detailed above. The distillation, as in the foregoing determinations, was continued nearly to dryness, and occupied twenty-five minutes. Before distillation was commenced, the temperature of the boiling liquid was found to be 166°.5, and at the close of distillation 167°. Applying the customary corrections to the average of these observations, viz. 166°.75, we obtain for the corrected boiling-point 169°.8.

Analysis. — 0.1944 gramme of the substance gave, by combustion in a stream of oxygen, 0.6366 of carbonic acid, and 0.1896 of water.

		Calculated.		Found.
Carbon,	C_{18}	108	90.00	89.31
Hydrogen,	H_{12}	12	10.00	10.84
		120	100.00	100.15

Determination of Vapor Density. —

Temperature of balance,	13°.5
Temperature of oil bath,	241°.0
Height of barometer,	769.5$^{mm.}$ at 9°
Increment of balloon,	0.4206
Capacity of balloon,	239 *c. c.*

Density of vapor found,	4.3019
Theory $C_{18}H_{12}$,	4.151

Hence it appears that the calculated density on the formula $C_{18}H_{12}$ is 0.151 *less* than that found by experiment. The calculated density on the formula $C_{20}H_{14}$, which has previously been assigned to this body, — although, as above stated, without an analysis or determination of vapor density, — is 4.645; which is 0.302 *greater* than that found by experiment. It will be observed that the difference between the density found and that calculated on the formula $C_{20} H_{14}$ is not only more than twice as large as the corresponding difference calculated on the formula $C_{18} H_{12}$, but that the error is reversed; being with $C_{20} H_{14}$ a *deficiency*, while with $C_{18} H_{12}$ it is an *excess*. This circumstance has to my mind a good deal of significance, as it goes strongly to show that the lower formula is the true one. For of the many vapor densities of hydrocarbons which I have determined, I have but rarely met with an instance in which the density found was not greater than the theoretical density. And I have usually observed that the excess of the experimental over the theoretical density is larger in proportion as the boiling-point of the body is higher, a fact which needs explanation. Wurtz* observed a similar difference between the determined and calculated vapor densities of bodies of the formulæ $C_n H_n$ and $C_n H_{n+2}$, which he accounted for on the ground that his preparations contained an admixture of bodies less volatile, the vapors of which would remain in the balloon, and increase the density. But I cannot accept this explanation for the substances here treated of, since they invariably distil without residue within a range of one degree of temperature. I would rather rely upon the supposition that the high temperature employed causes partial decomposition of the substance, which would be the more liable to occur the higher the boiling-point of the body. I do not, however, offer this as an explanation, but merely make the suggestion.

PART II.

HYDROCARBONS FROM OIL OF CUMIN AND CUMINIC ACID.

THE oil of cumin employed in this research was furnished by Messrs. Reed and Cutler, wholesale importers of drugs, etc. of Boston. The package bore the label of Eduard Büttner, manufacturer, of Leipzig, and purported to be a genuine preparation, answering in all of its obvious physical properties — odor, color, etc. — the description given of this oil by Gerhardt and Cahours† in their original memoir on this substance, who, it appears, also employed a commercial preparation. Its behavior in distillation left no doubt of its being a genuine article; and this was afterwards confirmed by treatment of the cuminole with fused potash, for the production of cuminic acid, its comportment with this reagent being in all respects identical with that described by Gerhardt and Cahours. Subjected to repeated series of fractionings by my process of fractional condensation already referred to, it gave, in addition to cymole and the residue of cuminole, a body boiling at about 155°, which so closely resembles oil of turpentine in odor, etc. as to be hardly distinguishable from the latter substance. The presence of this body may account for the very low boiling-point which Gerhardt and Cahours assigned to cymole, viz. 165°. The boiling-point of cymole was subsequently found by Gerhardt* to be 175°, but my own determination places it still lower by about 5°. It is evident, therefore, from a comparison of their own determinations, that the oil of cumin which they originally operated upon contained an oil boiling below cymole; and hence the finding of such an oil in that which I employed need not raise a doubt as to its being genuine. This lighter body is present in so small quantity as hardly to admit of its being detected, or at least identified, by the old process of fractioning; and its detection and isolation by the new process is but another illustration of the superior excellence of this method.

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* Bulletin de la Société Chimique de Paris, 1863, 309.

† Annales de Chimie et de Physique, 1841, 3e Série, I. 60.

1. OF THE BODY RESEMBLING OIL OF TURPENTINE.

Specific gravity, 0.8772 at 0°, and 0.8657 at 15°.

Determination of Boiling-point. — The quantity of material at command was too small to admit of attaining so high a degree of purity for this body as was desirable. The product obtained, however, distilled almost to dryness between 153°.4 and 155°.5. Taking the average of these observations, and applying the usual corrections, we obtain 155°.8 for the boiling-point of this body.

Analysis. — 0.2575 gramme of the substance gave, by combustion with oxide of copper, 0.8283 of carbonic acid, and 0.2766 of water.

		Calculated.		Found.
Carbon,	C_{20}	120	88.24	87.73
Hydrogen,	H_{16}	16	11.76	11.94
		136	100.00	99.67

Determination of Vapor Density. —

Temperature of balance,	16°
Temperature of oil bath,	211°
Height of barometer,	$758^{\circ}.4^{\mathrm{mm.}}$ at 14°
Increment of balloon,	0.4939
Capacity of balloon,	221 *c. c.*

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* Annales de Chimie et de Physique, 1845, 3^{e} Série, IV. p. 111.

Density of vapor found,	4.7281
Theory $C_{20} H_{16}$ = 4 volumes,	4.7028
Excess found,	.0253

The calculated density on the formula $C_{20} H_{14}$ is 4.635; which, compared with the density found, would increase the excess to 0.093. Although the determination agrees more nearly, indeed almost exactly, with the calculated density on the formula $C_{20} H_{16}$, the calculation on the formula $C_{20} H_{14}$ does not show a greater variation from the density found, than we have observed to be quite frequent with hydrocarbons of so high boiling-point; so that it may be questionable which of these formulæ is the true one. I cannot regard the determination of a vapor density as reliable for fixing the formula nearer than to within two equivalents of hydrogen. In the absence of opposing evidence, it will be wiser, however, to take the formula which agrees best with the results of experiment; at least until it shall be shown that the discrepancy between the calculated and observed vapor densities of bodies of high boiling-point, which appears to be so frequent, is nearly constant, or variable by some fixed law by which the amount of the error, in any given case, may be pretty nearly estimated. I shall therefore regard this body as having the formula $C_{20} H_{16}$, which is also better supported by the results of analysis. On account of its source, and close resemblance to oil of turpentine, I think of no better appellation for this body than cumo-oil of turpentine; thus adding another to the long list of isomers of the former substance, the chemical relations of which stand in so much need of being further studied.

2. CUMOLE.

This body was first obtained by Gerhardt and Cahours,* by the dry distillation of a mixture of six parts of crystallized cuminic acid, and twenty-four parts of caustic baryta. Abel † obtained the same result by substituting caustic lime for the baryta. His product, however, was found to boil 4° above that of Gerhardt and Cahours. My preparation was also made by the use of lime. Although the results of my experiments confirm the conclusions arrived at by Gerhardt and Cahours as to the composition of this body, yet the numerical results differ considerably from theirs. I have also observed some new facts regarding the formation of this body. They have described the reaction between the baryta and cuminic acid as being much more simple than my experiments seem to indicate. On this point they remark: "The formation of cumene is easily explained. In effect, the cuminic acid being represented by $C_{40} H_{24} O_4$, it appears that $C_4 O_4$, that is to say, 2 equivalents of carbonic acid, are retained by the baryta, while $C_{36} H_{24}$ are set free." *

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* Annales de Chimie et de Physique, 1845, 3e Série, IV. 87.

† Annalen der Chemie und Pharmacie, 1847, LXIV. 312.

$$C_{20} H_{12} O_2 = C_2 O_2 + C_{18} H_{12}.$$

In another place (p. 88) they remark, that "by suitably managing the heat, and employing no more than 6 gr. of cuminic acid at a time, no other products are ever obtained than those which we mention." † My experiments show that this reaction is by no means so simple as thus described. The crude product obtained from the mixture of lime and cuminic acid, when subjected to a simple distillation from a tubulated retort, was found to distil between 155° and 250°, leaving a residue at the latter temperature which became semi-fluid on cooling. The distillate thus obtained gave, by my process of fractional condensation, an oil boiling at 151°.1, and a residue at 170°. It is not improbable that the latter may prove to be mostly cymole, $C_{20} H_{14}$; but the quantity was too small to admit of pursuing this inquiry with the probability of deciding the question. There is evidence, however, that the product obtained by Gerhardt and Cahours was not simply pure cumole, as they described it, but a mixture of different bodies, which would necessitate a more complicated reaction than that which they assigned. Gerhardt and Cahours found the boiling-point of their cumole to be constant at 144°. Four years later, Gerhardt,‡ having occasion to make a very accurate determination of the boiling-point of this body, in connection with his research to find a law governing the boiling-points of the hydrocarbons, found its boiling-point to be 9° higher, viz. 153°, which is but 2° higher than my own determination. The disagreement between their determinations, it being so considerable, may be more reasonably accounted for on the supposition that they operated, in the first instance, upon a mixture of different bodies; and yet I cannot see how they could have obtained the product boiling below 150°. Additional evidence on this point will be found in the discrepancy which appears between their determination of the vapor density, and that calculated upon theory.

The specific gravity of my preparation of cumole was found to be 0.8792 at 0°, and 0.8675 at 15°.

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* "La formation du cumène s'explique aisément. En effet, l'acide cuminique etant représenté par $C_{40} H_{24} O_4$, on voit que $C_4 O_4$, c'est-a-dire 2 equivalents d'acide carbonique sont retenus par la baryte, tandis que $C_{36} H_{24}$ sont dégage." — Annales de Chimie et de Physique, 1841, 3e Série, I. 89.

† "En dirigeant la chaleur convenablement, et en n'employant pas plus de 6gr. d'acide cuminique à la fois, on n'obtient jamais d'autre produits que ceux que nous venons de nommer."

‡ Annales de Chimie et de Physique, 1845 (3), XIV. 107.

Determination of Boiling-point. — The quantity of material being quite small, this determination was made in a large test tube, with the usual precautions. It had not a perfectly constant boiling-point, the distillation ranging from 148°.4 to 151°.6. Applying the proper corrections to the mean of these observations, gives, for the boiling-point of cumole, 151°.1, which is doubtless a little too high from the impracticability of making a complete separation with the small quantity of material employed. If the boiling-point difference between cumole and cymole, for the difference of $C_2 H_2$ in their elementary formulæ, is 30°, as there is every reason to believe, then the boiling-point of cumole should be 150°, as I have found the boiling-point of cymole to be but a fraction under 180°.

Analysis. — 0.1700 gramme of cumole gave, by combustion with oxide of copper, 0.563 of carbonic acid, and 0.1557 of water.

		Calculated.		Found.
Carbon,	C_{18}	108	90.00	90.35
Hydrogen,	H_{12}	12	10.00	10.18
		120	100.00	100.53

Determination of Vapor Density. —

Temperature of balance,	17°
Temperature of oil bath,	203°
Height of barometer,	760.1$^{mm.}$ at 15°
Increment of balloon,	0.4428
Capacity of balloon,	232 *c. c.*

Density of vapor found,	4.2003
Theory $C_{18} H_{12}$ = 4 volumes,	4.151

This determination, as well as the results of analysis, confirms, therefore, the formula which Gerhardt and Cahours had assigned to this body. I had anticipated a different result from this, inasmuch as the hydrocarbon from coal-tar naphtha, which I have called *iso-cumole,* boiling at 170°, or nearly 20° higher than cumole from cuminic acid, — had been found, as I have shown above, to have the formula $C_{18} H_{12}$. I am forced to the conclusion, therefore, that these two bodies are isomeric, and belong to different series. A preliminary examination of their behavior with reagents indicates that their chemical properties are also different. These will be treated of on a future occasion, in Part III.

3. CYMOLE.

Notwithstanding that this body is so much more volatile than the cuminole with which it is associated in the oil of cumin, — there being a difference of 40° between their boiling-points, — Gerhardt and Cahours found it necessary to resort to chemical means, viz. treatment with fused potash, in order to isolate it. Being desirous of testing the efficiency of my process in effecting the separation, the preparation employed in this investigation was obtained by fractional condensation, this process having been found as effective in this as in other cases. This will appear by a comparison of the results obtained in the study of this body before and after treatment with concentrated sulphuric acid, which is also effective to remove cuminole.

Specific Gravity. —

At 0°, before treatment with $\dot{H}\dot{O}\ \dot{S}\dot{O}_3$,	0.8697
At 0°, after " " "	0.8724
At 14°, before " " "	0.8592

Determination of Boiling-point before Treatment with Sulphuric Acid. — The preparation was found to distil to dryness between 175°.8 and 177°. The temperature remained absolutely constant at 176° during the lapse of ten minutes, and occupied fifteen minutes in rising from 176° to 176°.5. Taking the mean of the former numbers, viz. 176°.4, and applying the proper corrections for pressure, etc., we obtain 179°.5 for the boiling-point of cymole.

After Treatment with Sulphuric Acid. — The preparation distilled to dryness between 176° and 177°, the temperature remaining thirteen minutes constant at 176°.3, indicating that no essential change in the boiling-point had been produced by the acid treatment. It was nevertheless evident that some impurity was being removed by the acid, as the first portions of the latter became dark-colored and thickened on being agitated with the oil. Successive portions of acid were therefore employed, until it ceased to produce any marked effect.

Analysis before Treatment with Sulphuric Acid. — 0.1589 gramme of cymole gave, by combustion in a stream of oxygen gas, 0.5200 of carbonic acid, and 0.1532 of water.

		Calculated.		Found.
Carbon,	C_{20}	120	89.55	89.25
Hydrogen,	H_{14}	14	10.45	10.71
		134	100.00	99.96

After Treatment with Sulphuric Acid, and Distillation in Vacuo. — 0.1623 gramme of cymole, by combustion in a stream of oxygen gas, gave 0.5324 of carbonic acid, and 0.1561 of water.

		Calculated.		Found.
Carbon,	C_{20}	120	89.55	89.46
Hydrogen,	H_{14}	14	10.45	10.68
		134	100.00	100.14

The removal of impurity by treatment with sulphuric acid had therefore hardly a sensible effect on the results of analysis.

Determination of Vapor Density before Treatment with Sulphuric Acid. —

Temperature of balance,	11°
Temperature of oil bath,	259°
Height of barometer,	$740.6^{\text{mm.}}$ at 5°
Increment of balloon,	0.4446
Capacity of balloon,	239 *c. c.*

Density of vapor found,	4.742
Theory $C_{20}H_{14}$ = 4 volumes,	4.6351

After Treatment with Sulphuric Acid. —

Temperature of balance,	25°.5
Temperature of oil bath,	255°
Height of barometer,	$760^{\text{mm.}}$ at 26°
Increment of balloon,	0.4647
Capacity of balloon,	232 *c. c.*

Density of vapor found,	4.7536
Ditto before treatment with $HO\,SO_3$,	4.742
Difference,	.0116

The results of the two determinations are therefore almost identical.

A comparison of the above results with those obtained in the study of isocumole, the body from coal-tar naphtha boiling at 170°, will show that the two bodies are far from being the same substance, as Mansfield assumed, and that they have a constitutional difference of C_2H_2, and therefore doubtless belong to different series.

NOTE. — I had hoped to be able to present on this occasion the results of the study of some of the more important reactions of the hydrocarbons treated of in the preceding pages, — at least, of those in regard to which I have differed from my predecessors; but as this work is yet incomplete, and as I am at present occupied with the study of other substances of more immediate interest, I will defer this branch of the subject for future consideration, in Part III. I may here remark, however, that the behavior of these bodies with reagents is such as to strengthen the conclusions already expressed in regard to them.

II.

On the Influence of $C_2 H_2$ *upon the Boiling-points in Homologous Series of Hydrocarbons, and in some Series of their Derivatives; with Critical Observations on Methods of taking Boiling-points.*

It is well known that we are indebted to H. Kopp* for the discovery of certain definite relations existing between the chemical constitution and some of the physical properties of homologous liquid bodies. Of these, one of the most important is that of a uniform difference between the boiling-points of the contiguous members of an homologous series, corresponding to the uniform difference in their elementary constitution. Kopp has shown by numerous examples, that, as a general rule, in those series which are characterized by a common elementary difference of $C_2 H_2$ between the members, in the order of the series, the corresponding difference of boiling-point is about 19° C.; hence, that the difference between the boiling-points of any two members of such a series is $x . 19°$ for a difference of $x\ C_2 H_2$ in the elementary formulæ. In the earlier observations on this subject, this relation between the boiling-points and formulæ was found so nearly constant in the different series examined, that any deviations from this apparent general law were referred, not unreasonably, to assumed inaccuracies in the determination of the boiling-points of the bodies compared. But the more recent and extended generalizations of Kopp† have led him to point out several exceptional series, in which the boiling-point difference is greater, and others in which it is less, than 19° for an elementary difference of $C_2 H_2$. That there are such exceptional series is confirmed in a very decisive manner by my own observations, as I shall proceed to show. My determinations make the boiling-point differences in some cases so much larger than those of other observers as to leave no room for doubt on this point; especially if the comparative value of these determinations be duly estimated with reference to the more reliable character to which the preparations are entitled, on account of the more efficient means which I have employed for separating the liquids. Since Kopp first called the attention of chemists to this subject, different theories have from time to time been advanced by Schröder, Löwig, Gerhardt, and others, and supported by laborious research and observation. It will be interesting to examine some of these theories in the light of the new facts which I am about to present. Schröder,* not satisfied with Kopp's explanation of the discrepancies between the observed and theoretical boiling-points, on the ground of errors of determination of the former, argues that the influence of $C_2 H_2$ on boiling-points is variable in different series according to the peculiar nature of the $C_2 H_2$ in each case. He regards organic compounds for the most part made up of radicals, which he calls "components," of which he makes seven. Three of these are composed of carbon and hydrogen, viz.: —

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* Annalen der Chemie und Pharmacie, 1842, XLI. 79, 169; 1845, LV. 177, etc.

† Annalen der Chemie und Pharmacie, 1855, XCVI. 2.

Formyl = $(C_4 H_2)$ — ("$C_4 H_4$") — which is supposed to raise the boiling-point of a substance 52° C.

Methylen = $(C_2 H_2)^m$ — "$(C_2 H_4)^m$" — which is supposed to raise the boiling-point of a body 21°.

Elayl = $(C_2 H_2)^e$ — "$(C_2 H_4)^e$" — which is supposed to raise the boiling-point 17°. Subsequently (Pogg. Ann., 64, 101) the latter number was changed by Schröder to 16°.

A fourth component was made up of a double atom of hydrogen, (H_2) — "(H_4)" —, which was supposed to lower the boiling-point 3°; but this also was afterwards changed to 10° (Pogg. Ann., 64, 372). (The other three components, having no direct bearing on the hydrocarbons, are omitted.) By means of these components Schröder (Pogg. Ann., 62, 188) proposed to calculate the boiling-points of different substances in the following manner. Having estimated the sum of the influence of the different components of a body, the number 70 was in all cases to be deducted. Subsequently Schröder† was led to substitute, in these calculations, the influence of the separate elements for that of the components. Each double atom of carbon (C_2) was estimated to raise the boiling-point of a compound 31°; and each double atom of hydrogen (H_2) to lower it 10°. As in the former case, the number 70 was to be deducted from the sum of the influences of the different elements contained in the compound, to give the true boiling-point. Example: calculation of the boiling-point of benzole, $C_{12} H_6$; $C_{12} = 6\,C_2$; $31° \times 6 = 186°$; $H_6 = 3\,H_2$; $-10° \times 3 = -30°$; $186° - 30° - 70° = 86°$ = the calculated boiling-point of benzole by this method; which agrees exactly with the latest determination at the date of Schröder's memoir.

Löwig‡ estimates the influence of the elementary atoms on the boiling-point differently from Schröder; and obtains numbers such that, to find the boiling-point of a compound it is only required to add together the numbers corresponding to the elementary atoms which it contains, without deducting from this sum a constant number, as by Schröder's method. According to Löwig's theory, one atom of carbon (C) raises the boiling-point 38°.4, and one atom of hydrogen (H) lowers it 29°.2; these numbers being for carbon nearly two and one half times, and for hydrogen nearly three times as great, as those of Schröder. Gerhardt,* in a special paper "On the Boiling-point of the Hydrocarbons," observes that "The boiling-point of the hydrocarbons appears to obey a very simple law, according to which it is raised or depressed a certain number of degrees, corresponding to the number of equivalents of carbon or hydrogen contained in its equivalent." † From a comparison of the boiling-points and formulæ of several well-known hydrocarbons, the determinations of which were repeated with special care for this purpose, Gerhardt finds that the addition of C_2 to the molecule of an hydrocarbon raises its boiling-point 35°.5, and that the addition of H_2 lowers it 15°. The boiling-point of a body is calculated from these numbers by comparing its formula with oil of turpentine, $C_{20} H_{16}$, as a standard, the boiling-point of which is taken at 160° C. Example: cumole (from cuminic acid) has the formula $C_{18} H_{12}$; hence it contains C_2 less than oil of turpentine; therefore 35°.5 must be deducted from 160° (the boiling-point of oil of turpentine), which leaves 124°.5; but as the cumole contains $2 H_2$ less than oil of turpentine, $15° \times 2 = 30°$ is to be added to the above remainder; thus $124°.5 + 30° = 154°.5$, the calculated boiling-point of cumole. Gerhardt's direct determination was 153°, which very nearly coincides with his theory.

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* Poggendorff's Annalen, 1844, LXII. 184, 337.

† Poggendorff's Annalen, 1845, LXIV. 367; 1846, LXVII. 45.

‡ Poggendorff's Annalen, 1845, LXIV. 250.

It would be foreign from my purpose on the present occasion to consider these different hypotheses, or even the empirical law of Kopp, beyond their special relation to the boiling-points of the hydrocarbons, and such other series, derivatives from the hydrocarbons, as have been made the subjects of my own experiments. Anything more than this would be merely speculative. The want of more accurate determinations of boiling-points as essential to safe and reliable deductions and generalizations on this question, has frequently been observed. The need of this will be made strikingly apparent by comparison of my results with those of previous observers. Indeed, if my determinations may be taken as a criterion, — which, considering the nature of the materials operated upon, might not be quite fair, — the inaccuracies of the boiling-points which have hitherto been published are probably so numerous, and in many cases so considerable, as to make it appear almost useless to attempt further generalizations upon those unreliable data. It may be hoped, however, that the superior means which my process furnishes for separating mixtures of liquids, will lead to the accumulation of reliable facts of sufficient number and variety for a profitable review of this question in its different bearings, which, from its importance, it clearly merits.

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* Annales de Chimie et de Physique, 1845, 3e Série, XIV. 107.

† "Il parait que le point d'ébullition des hydrogène carbonés est soumis à une loi fort simple, d'après laquelle il s'élèverait ou s'abaisserait d'un certain nombre de degrés suivant le nombre des équivalents de carbone ou d'hydrogène renfermés dans leur équivalent."

The frequent inaccuracy of the determinations of boiling-points, upon which Kopp has justly laid so much stress, may, I think, be more reasonably attributed, at least in a majority of cases, to a want of purity in the substances themselves, rather than to a neglect of the precautions and corrections which he recommends to be observed in such determinations; although errors as great as those mentioned by Kopp* may doubtless occur, and in the particular instances which he had in mind may have occurred from the cause which he assigned for them. It should be borne in mind, however, that these errors, in the case of an impure substance, may be compensating errors; or, on the other hand, they may go to increase that which would arise from impurity.

That the conditions under which my results have been obtained may be clearly understood, and hence the value of these results fairly estimated, in comparison with those of others, I shall endeavor, as I proceed with these researches, to specify, in sufficient detail, the processes which I have employed. Having, in the memoir previously referred to, described the process by which the hydrocarbons were separated, the special object of this paper only requires, in this regard, that I should add a description of the method employed in determining the boiling-points of these bodies, which has already been partially given in the foregoing memoir, when treating of the boiling-point of benzole.

Of the Method of determining Boiling-points. — I use for this purpose a small tubulated glass retort, and usually operate on about 150 *c. c.* of the liquid. The thermometer extends into the liquid, even nearly to the bottom of the retort, taking care that the bulb shall not come in contact with the glass, but remain free in the liquid. To prevent abnormal elevation of temperature from adhesion to the glass, — which I have observed in some instances, when operating on impure hydrocarbons, to amount to several degrees, — I introduce pieces of sodium, instead of platinum, as it seems to serve at least as well for this purpose, and at the same time tends to preserve the purity of the material. Sodium has also this advantage over platinum for hydrocarbons, viz. that it does not lose its virtue by use, so long as any of it remains; platinum, on the contrary, being liable, especially if the liquid is not quite pure, to become after a while slightly coated, and its efficiency thus impaired.*

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* "Bestimmung des Siedepunkts." Poggendorff's Annalen, 1847, LXXII. 38.

Except for low temperatures, the retort rests on a piece of wire gauze laid over the ring of an iron lamp-stand, and is heated with a small gas-flame. When operating on liquids of low boiling-point, I have observed the liability of the thermometer to be considerably affected by the ascending current of hot air striking the sides of the retort above the level of the liquid, thus causing an elevation of several degrees of temperature. To prevent this, I proceed as follows. For low temperatures, and yet above the common temperature, I place upon the gauze on which the retort is to stand, a screen of felt or thick woollen paper, which has been provided with a hole in the centre about two inches in diameter. This screen extends several inches from the sides of the retort, and has been found effectual for the purpose.

For temperatures below the common temperature, the retort is set in a water-bath containing ice-water, the temperature of the bath being gradually raised by means of a small gas-flame.

As is customary, in order to ascertain the temperature by which to calculate the correction for the upper column of mercury, a thermometer is attached, by means of elastic bands, to the side of the thermometer in the retort; the bulb being placed, during ebullition, midway between the centre of the cork and the upper extremity of the mercurial column. And, as usual, a paper screen, closely fitting the thermometer, is placed across at the top of the cork to shield the upper column of mercury from the direct influence of the ascending heat.

I have observed that it often requires considerable time — variable according to its length and the thickness of the glass spindle — for that part of the thermometer above the retort to acquire the highest temperature which the boiling liquid can communicate to it. During this time the thermometer evidently is not in a fit state for an observation. While this gradual change in the condition of the thermometer is taking place, it is desirable, for obvious reasons, that no vapors should escape from the retort. I therefore proceed as follows. The retort, the neck of which has previously been wrapped with a wet cloth, is placed in such a position that the neck shall slightly incline towards the body of the retort. If necessary, some pieces of ice, which will adhere firmly to the cloth, may be laid along the neck to insure complete condensation of the vapors during ebullition. While the retort is in this position, ebullition is continued for considerable time, until it ceases to have any effect on the height of the mercury in the thermometer. The lamp being now removed for the moment, the neck of the retort is turned down, and quickly connected with a Liebig condenser. The lamp being now replaced, the distillation is commenced. So soon as the mercury in the thermometer shall have become constant, which will now occupy but a few seconds, the temperatures by the retort thermometer and the side thermometer are carefully noted, and also the time at which these observations are made. During the distillation, which is continued nearly to dryness, the readings of the thermometers and of the watch are noted at regular intervals, or so often as any appreciable variation of the retort thermometer shall have taken place. The average of the several observations, or of those corresponding to the longer intervals of time, applying the corrections for atmospheric pressure and for the upper column of mercury, according to Kopp,* is taken for the true boiling-point. I have generally obtained the hydrocarbons so pure that the whole quantity operated upon would distil within the range of 1° of temperature, and not unfrequently within 0°.5. In a few cases, however, when the quantity of material at command would not permit of the attainment of so high a degree of purity, the distillation would range over two or three degrees; in such cases I have generally taken the average of the temperatures corresponding to the longest interval of time, as probably representing more nearly the true boiling-point of the body. In stating my results, however, I shall give the limits of temperature within which the distillation was effected. The thermometers employed in the determinations were the best that I could obtain from Fastrè of Paris; for the temperatures below 100° the instrument used was calibrated, and the scale divided into fifths of a degree. The determinations above 100° were all made with one thermometer.

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* For common use in fractioning, when not desirable to use sodium, I have found pieces of coke to be more effectual and much more durable than platinum. Not unlikely it would be found equally preferable to platinum for general use in taking the boiling-points of liquids in which sodium could not be employed. It is certain that nothing could operate better than coke for the nitro-compounds and alkaloids derived from benzole and its homologues.

The method just described differs in some respects from that of Kopp. He objects to the practice of taking boiling-points with the thermometer bulb immersed in the liquid,† on the ground that the thermometer in this condition hardly ever indicates a constant temperature, the end of the mercurial column being in a state of motion. He states that a boiling-point taken in this manner may lie several degrees above that found with the thermometer bulb in the vapor. As bearing on this point, I propose, a little farther on, to give the results of a few experiments and observations, which, with others of similar character, have induced me to depart from the now more common custom of taking boiling-points with the thermometer bulb in the vapor.

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* Poggendorff's Annalen, 1847, LXXII. 38.

† "Lässt man die Kugel des Thermometers in die siedende Flüssigkeit tauchen, so zeigt fast nie das Instrument eine constante Temperatur, sondern das Ende des Quecksilberfadens ist in stetter hüpfender oder zittender Bewegung; der auf diese Art gefundene Siedepunkt kann nur mehrere Grade höher liegen, als der, welcher gefunden wird, wenn sich die Kugel des Thermometers in dem Dampf der siedenden Flüssigkeit befindet."

Under normal conditions, the temperature of the boiling liquid and that of the vapor evolved should be the same. The only disturbing influence which appears to have been specially dwelt upon as likely to alter these conditions in the taking of boiling-points, is the liability of some liquids to adhere to the surface of the glass in such a manner as to produce abnormal elevation of temperature, generally attended with irregular ebullition, and consequent fluctuation of the thermometer. To remedy this it is usual to introduce pieces of platinum; iron filings, coal, etc., have also been employed. As above remarked, pieces of coke — or, when admissible, sodium — are found to be more surely effectual with hydrocarbons than platinum. Indeed, during more than three years of experience and careful observation upon a large number of hydrocarbons, I have not yet met with a single instance in which irregular ebullition and its consequent disturbing influence upon the boiling-point might not be completely prevented by these means. Although I cannot, of course, go so far as to say that equally satisfactory results would be obtained with other liquids by the use of coke, it is nevertheless my belief that in a majority of instances such would be the case.

I have dwelt upon this point for the reason that the objections to the custom of taking boiling-points with the bulb in the vapor, appear to be even greater than those which Kopp has raised against the opposite course of placing the bulb in the liquid, as I shall proceed to show. It therefore becomes a matter of some importance that the objections to one or the other custom should be removed; and I think it will be found easier to overcome the objections to placing the bulb in the liquid, as I have done in the case of many hydrocarbons, even if coke shall not be found equally efficient with most other liquids.

My experience has shown that, when irregular ebullition is effectually prevented, the temperature of the vapor from a boiling liquid is more liable to lead to an erroneous determination of the boiling-point, than the temperature of the liquid itself. The reasons for this are, first, that the vapor is liable to become superheated by the hot air from the flame coming in contact with the sides of the retort above the surface of the liquid; second, that, with the bulb in the vapor, the thermometer is more liable to sudden depression from currents of cool air passing over the retort.

If the bulb be in the vapor, the occurrence of either of these disturbing influences would then affect the principal mass of the mercury in the thermometer; while, on the contrary, if the bulb were in the liquid, only the small quantity of mercury in the stem of the thermometer would be subjected to these influences; the liquid then serving as a regulator, and reducing the error from these sources to a minimum. Fluctuations from currents of cold air are comparatively slight, and more easily prevented than those from overheating the vapor. The latter is the more likely to occur the lower the boiling-point of the liquid, or when the quantity of liquid in the retort is small. I have, however, observed from this cause an elevation of 3°–4° in distilling a body boiling as high as 98° C., without an unnecessarily large flame. But the liquid in this instance was pretty low in the retort.

In the case of liquids boiling below the common temperature, it seems indispensable that the bulb of the thermometer should be placed in the liquid. As evidence of this I will here state the results of observations made while occupied in fractioning some exceedingly volatile products from American petroleum.

Experiment 1. — The liquid operated upon boiled at so low a temperature that the distillation was effected by the heat of the surrounding atmosphere. The distillation was conducted in a flask, and the bulb of the thermometer placed in the vapor. The flask was attached to my condensing apparatus, including the "refrigerator, B, Fig. 2."* The temperature of the condensing-worm contained in the "elevated bath, *aa*, Fig. 2,"* and also that of the "first receiver, *k*, Fig. 2,"* was 11°.5. The temperature of the "cold bath, *ii*, Fig. 2,"* was 11°. The condenser in "the refrigerator, B," and the "second receiver," were cooled in a mixture of ice and salt. With the liquid boiling steadily from several points on the bottom of the flask, and the condensed product from the distillation running well from the refrigerator into the "second receiver," not a drop was condensed in any of the apparatus intervening between the flask and the "second receiver," although this part of the apparatus was cooled, as already stated, to about 11°. The temperature of the vapor in the flask at this time was 18°.5, or only 2°.5 below the temperature of the laboratory. These observations show that the liquid was boiling at a temperature considerably below that indicated by the thermometer in the vapor. Additional evidence of this was furnished by the fact that, during the distillation, the exterior of the flask, from the bottom to about one quarter of an inch above the surface of the liquid, was thickly covered with water condensed from the atmosphere, resembling heavy dew; while above, the sides of the flask were perfectly dry. It was these observations which first directed my attention to the fact that the temperature of the vapor could not in all cases be depended upon for the true boiling-point of a liquid, and naturally led me to make other experiments with special reference to this question.

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* See Memoir "On Process of Fractional Condensation," Memoirs of the American Academy, 1864.

Experiment 2. — The conditions of this experiment were somewhat different from those of the first. The liquid operated upon was the extremely volatile product collected in the "second receiver" of Experiment 1. The flask employed was smaller, and provided with two thermometers; the bulb of one of these was placed in the liquid, and that of the other in the vapor. The flask stood in a water-bath containing ice-water; this bath was also provided with a thermometer. The temperature of the ice-water bath was very gradually raised by means of a small flame from a Bunsen's burner. Temperature of the laboratory, 20° C. Observations during the distillation: —

	1.	Temperature of the water-bath,	10°
		" " boiling liquid,	8°
		" " vapor,	18°.5
	2.	Temperature of the water-bath,	12°
		" " boiling liquid,	9°
		" " vapor,	18°
15 minutes later.	3.	Temperature of the water-bath,	18°
		" " boiling liquid,	10°
		" " vapor,	14°
10 minutes later.	4.	Temperature of the water-bath,	20°
		" " boiling liquid,	12°
		" " vapor,	19°
20 minutes later.	5.	Temperature of the water-bath,	23°
		" " boiling liquid,	15°
		" " vapor,	19°

Experiment 3. — The subject of this experiment was a liquid which I had separated from the most volatile product of the re-distillation, on a manufacturing scale, of the crude benzole obtained in the distillation of coal-tar. The apparatus employed was essentially the same as that used in Experiment 1, with the addition of the extra thermometers, as in Experiment 2. The condensing-worm in the "elevated bath," and that in the "cold bath," and also the "first receiver," were all cooled in pounded ice. The condenser in the "refrigerator," and also the "second receiver," were both cooled in a mixture of ice and salt. The retort, which stood in a small copper bath containing pounded ice, was charged with about 250 *c. c.* of the liquid, which had been previously cooled in a mixture of ice and salt. Temperature of the laboratory, 16° C. Observations during the distillation : —

	1.	Temperature of the retort-bath,	0°
		“ “ boiling liquid,	0°.6
		“ “ vapor,	13°.5
45 minutes later.*	2.	Temperature of the retort-bath,	0°
		“ “ boiling liquid,	1°.3
		“ “ vapor,	12°.2
15 minutes later.	3.	Temperature of the retort-bath,	6°
		“ “ boiling liquid,	1°.8
		“ “ vapor,	12°.6
30 minutes later.	4.	Temperature of the retort-bath,	11°
		“ “ boiling liquid,	3°.8
		“ “ vapor,	12°.4
30 minutes later.	5.	Temperature of the retort-bath,	14°.5
		“ “ boiling liquid,	7°.3
		“ “ vapor,	13°.8

The apparent inconsistency that the temperature of the boiling liquid should be above that of the heating medium, — viz. an ice-bath — which continued during the first forty-five minutes of the experiment, is to be explained by the fact that there was a long column of mercury, above the surface of the liquid, which was subjected to the heating influence of the vapor. I would further remark that the gradual elevation of the boiling-point, as indicated by the thermometer in the liquid, is also only apparent, and is due to the gradual uncovering of the bulb as the liquid was distilled off. At the close of the experiment only about one fifth of the bulb, which unfortunately was a long one, was under the surface of the liquid. That this is the true explanation is evinced by the fact that during the experiment not a drop of liquid was observed to fall back into the retort from the “elevated condenser,” although this was a tube ten feet in length, and cooled to the temperature of 0°.

I will now proceed to give my determinations of the boiling-points of various hydrocarbons, and of some of their derivatives, and then pass directly to consider the bearing of these results on the question concerning the increment of boiling-point for the addition of C_2H_2 in homologous series.* The data for these considerations may be more conveniently arranged in tabular form, exhibiting at once, in serial order, the formulæ, boiling-points, elementary difference, and the corresponding difference of boiling-point.

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* From this point the temperature of the retort-bath was gradually raised by means of a small gas-flame.

1. *Of the Hydrocarbons obtained from Pennsylvania Petroleum.*

1st Series.

Formula.	Boiling-point.	Elementary Difference.	Difference of boiling-point found.	Range of Temperature within which the substance would all distil.†
	°		°	°
C_8H_{10}	0.0 (?)			
$C_{10}H_{12}$	30.2	C_2H_2	30.2	1.5
$C_{12}H_{14}$	61.3	C_2H_2	31.1	0.8
$C_{14}H_{16}$	90.4	C_2H_2	29.1	1.0
$C_{16}H_{18}$	119.5	C_2H_2	29.1	1.0
$C_{18}H_{20}$	150.8	C_2H_2	31.3	0.8
			150.8 ÷ 5 = 30°.16	

Average increment of boiling-point for the addition of C_2H_2 = 30°.16.

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* In considering this question I shall include the boiling-points of the substances which I have separated from Pennsylvania petroleum, and the oil distilled from Albert coal; reserving for a subsequent memoir all other facts which have been derived from the study of these bodies.

† The ranges of temperature given in this and in the corresponding columns of the following tables, are for the purpose of showing the impossibility of there having been any essential error in the determinations of the boiling-points; as is evinced by the fact, in each case, that the whole product was found to distil without residue within such narrow limits. With so small a range of temperature, it is evident that it would make no practical difference whether either extreme or the mean of the observations be taken for the boiling-point.

The fact that these substances distil without residue within so short a range of temperature, is also of much value as proof of the existence of the two parallel series in petroleum and in coal-oil, with boiling-points so near together; [as shown by comparison of the boiling-points of the first with the second series from petroleum; and also of the two corresponding series from Albert coal-oil]; especially if this is considered in connection with the fact, so far as my experience goes, that the quantities of material in one series are generally about equal to those in the other.

That no erroneous conception may be formed as to the degree of purity of the substances treated of in this and in the following tables, from a mere inspection of the *ranges* of temperature here given; and in order that the almost absolute constancy of the boiling-points, in most cases, may not be overlooked, I would refer to the preceding memoir for further details concerning the boiling-points of such of these bodies as are therein treated of. For example, it will be found under the head "Determination of boiling-point" of benzole, that in the distillation it required 50 minutes for the temperature to rise 0°.2; while in one of the following tables it will be seen that the *range* of temperature within which the benzole distilled to dryness was found to be 0°.8. Likewise, by reference to the "Determination of boiling-point" of toluole it will be observed that it was found to boil absolutely constant 48 minutes; while the *range* of temperature given in the table referred to is 0°.7. In such cases as these, the slight rise of temperature which takes place just before going to dryness, is doubtless to be attributed to superheating of the vapor, in consequence of there being so small

2D SERIES.*

Formula. (?)	Boiling-point.	Elementary difference.	Difference of boiling-point found.	Range of Temperature within which the substance would all distil.
	°		°	°
$C_8 H_{10}$	8-9			
$C_{10} H_{12}$	37.0	$C_2 H_2$	29.0	0.4
$C_{12} H_{14}$	68.5	$C_2 H_2$	31.5	0.6
$C_{14} H_{16}$	98.1	$C_2 H_2$	29.6	1.2
$C_{16} H_{18}$	127.6	$C_2 H_2$	29.5	1.5

119.6 ÷ 4 = 29°.9

Average increment of boiling-point for the addition of $C_2 H_2$ = 29°.9.

3D SERIES. (*Not completed.*)

Formula.	Boiling-point.	Elementary difference.	Difference of boiling-point found.	Range of Temperature within which the substance would all distil.
	°		°	°
$C_{20} H_{20}$	174.9			1.7
$C_{22} H_{22}$	195.8	$C_2 H_2$	20.9	1.5
$C_{24} H_{24}$	216.2	$C_2 H_2$	20.3	2.2

41.2 ÷ 2 = 20°.6

Average increment of boiling-point for the addition of $C_2 H_2$ = 20°.6.

2. *Of the Hydrocarbons obtained from Albert Coal.*

1ST SERIES. (*Not completed.*)

Formula.	Boiling-point.	Elementary difference.	Difference of boiling-point found.	Range of Temperature within which the substance would all distil.
	°		°	°
$C_{10} H_{12}$				
$C_{12} H_{14}$	59.9	$C_2 H_2$		1.5
$C_{14} H_{16}$	90.6	$C_2 H_2$	30.7	0.5
$C_{16} H_{18}$	119.7	$C_2 H_2$	29.1	0.5

59.8 ÷ 2 = 29°.9

The average boiling-point difference, in this series, for the addition of $C_2 H_2$, is, therefore, 29°.9.

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a quantity of liquid in the retort. Similar instances of absolute constancy of boiling-point as those just cited, might be given from among the products in either series from petroleum and Albert coal; which the *ranges* of temperature given in these tables do not indicate.

* I am somewhat in doubt whether the bodies composing this series and the 2d Series from Albert coal have the formula $C_n H_{n+2}$ as here represented, there being some indication that they contain less of hydrogen. For the purpose for which they are now presented, it is immaterial which formula is employed, as the common elementary difference and the boiling-point differences would remain the same; the solution of this question is therefore deferred for a subsequent memoir.

2D SERIES. (*Not completed.*) [*]

Formula. (?)	Boiling-point.	Elementary difference.	Difference of boiling-point found.	Range of Temperature within which the substance would all distil.
	°		°	°
$C_{10}H_{12}$				
$C_{12}H_{14}$	68.0	C_2H_2		1.0
$C_{14}H_{16}$	98.5	C_2H_2	30.5	0.6
$C_{16}H_{18}$	125.1	C_2H_2	26.6	

57.1 ÷ 2 = 28°.6

Average boiling-point difference = 28°.6.

3. *Of Hydrocarbons obtained from Coal-tar Naphtha.*

Name of Substance.	Formula.	Boiling-point.	Elementary difference.	Difference of boiling-point found.	Range of Temperature within which the substance would all distil.
		°		°	°
Benzole,	$C_{12}H_6$	80.0			0.8
Toluole,	$C_{14}H_8$	110.3	C_2H_2	30.3	0.7
Xylole,	$C_{16}H_{10}$	139.8	C_2H_2	29.5	0.4
Isocumole,	$C_{18}H_{12}$	169.9	C_2H_2	30.1	1.0
				89.9	

Average increment of boiling-point for the addition of C_2H_2 = 89.9 ÷ 3 = 29°.97.

4. *Of Cumole from Cuminic Acid, and Cymole from Oil of Cumin.*

Name of Substance.	Formula.	Boiling point.	Elementary difference.	Difference of boiling-point found.	Range of Temperature within which the substance would all distil.
		°		°	°
Cumole,	$C_{18}H_{12}$	151.1			3.6
Cymole,	$C_{20}H_{14}$	179.6	C_2H_2	28.5	1.2

With only a single exception, the results presented in the above tables point clearly to 30° as the common increment for the addition of C_2H_2 in homologous series of hydrocarbons. Indeed, leaving out of the calculation the third series from petroleum (having the general formula C_nH_n), — which must remain anomalous, — and also the products from oil of cumin, the average of all the other boiling-point differences is 29°.75. The few individual variations from the number 30°, rarely exceeding a single degree, may reasonably be attributed to errors of the thermometer (especially in case of temperatures above 100°), or in some instances to a want of purity of one of the compared substances; which latter cause I doubt not is the case with the body from petroleum boiling at 37°, as upon this body I had bestowed less labor in fractioning than upon most of the others, on account of the extreme volatility and consequent loss of the substance, by which the quantity had become so much reduced that I could ill afford further loss. In the case, also, of cymole from oil of cumin, and cumole from cuminic acid, in which the boiling-point difference varies only 1°.5 from the common difference of 30°, the want of perfect agreement may be fairly accounted for by the fact that the quantity of cumole at command was too small to admit of continuing the process of fractioning far enough to obtain perfect constancy of boiling-point. In consequence, also, of the quantity being so small, the *determination* of the boiling-point of cumole is less reliable, as this had to be conducted in a test-tube. It came into full ebullition at 148°.4, the temperature rising gradually to 151°.6 (observed temperatures), at which latter temperature it had distilled nearly to dryness. The distillation occupied thirteen minutes in passing over the range of three degrees. The average of the extremes, with the usual corrections for pressure, &c., was taken for the boiling-point. Abel,* who probably operated on a larger quantity, found the boiling-point of cumole to be 148°. It does not appear that he applied the corrections for pressure and the upper column of mercury. I do not doubt that the true boiling-point of this body will be found to be 150°, which would establish the difference of 30° between it and cymole.

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[*] See foot-note on the preceding page.

I would here remark that this difference of 30° for the addition of $C_2 H_2$ was first observed while engaged in fractioning Pennsylvania petroleum, and the oil from Albert coal, — substances the most difficult to separate, on account of the presence in each of two parallel series of constituents, whose boiling-points lie so near together.

As no one had preceded me in the investigation of these substances, my mind was as far as possible unbiased as to the boiling-points of the constituents of these mixtures. I was, however, aware of the beautiful relation between elementary constitution and boiling-point which Kopp had discovered, and familiar with the fact that the more recent investigations had shown the boiling-point difference among homologous hydrocarbons to be about 22°.5. If there was any one thing which more than another tended to bias me, it was the recent work of Church† on the boiling-points in the benzole series, in which he made the boiling-point difference invariably 22° and a fraction, a number varying but 3° from the theory of Kopp. Soon after the publication of Church's results, however, Kopp‡ accepted the number 22°.5 as about the boiling-point difference in this series, therefore regarding it as one of the exceptional series in which the boiling-point difference is greater than 19°. The work of Church had certainly the appearance of having been performed with great care, conducting to a beautiful harmony of results. My confidence in his determinations of boiling-points was increased not a little by his alleged discovery in coal-naphtha of xylole, boiling at 126°.2, indicating a more thorough analysis of this naphtha than those which had been previously published. This body, the supposed middle member of the benzole series, had up to that time been regarded as wanting in coal-tar naphtha, although all of the other members, above and below it, were found to be present, — an anomaly not easily reconciled with any plausible theory in regard to the formation of these bodies. In view of these circumstances, therefore, I was naturally led, from analogy, to anticipate that the boiling-point difference among the hydrocarbons from petroleum and Albert coal would not vary much from 20°. Not being able, however, to reconcile with previous facts and theories on this subject, the indications which were being gradually unfolded by my seemingly unerring process of separation, I was compelled to lay aside all bias, and to regard these indications as pointing unmistakably to a much greater difference of boiling-point for the addition of $C_2 H_2$ than had previously been supposed to exist in this class of substances.

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* Annalen der Chemie und Pharmacie, 1847, LXIII. 308.

† Philosophical Magazine, 1855, (4.) IX. 256.

‡ Annalen der Chemie und Pharmacie, 1855, XCVI. 29.

Having finally established beyond question the common difference of 30° for the addition of $C_2 H_2$ among the hydrocarbons from Albert coal and petroleum (the third series from petroleum, with the difference of 20°, had not then been reached), I began to surmise that this difference might be found to be common among all other series of hydrocarbons. In this connection my mind naturally reverted to the earlier determinations of the boiling-points of the members of the benzole series, some of which, especially those of benzole and toluole, which had been more studied than the others, indicated strongly that 30° might prove to be the true difference for the addition of $C_2 H_2$ in this series. My confidence in Church's determinations thus began to diminish, and finally I undertook to make a thorough analysis of coal-tar naphtha, the results of which are given in Table 3. As there shown, the boiling-point difference in the benzole series is also 30°, and the number of its members is reduced to four, in place of five, as alleged by Church.

This difference of 30°, thus shown to be so common with the hydrocarbons, is so much larger than the difference of 19° which Kopp had found so frequent in other classes of substances, that the discrepancy cannot be regarded otherwise than as conclusive evidence, if such were wanting, that all liquid bodies do not obey the same law in this regard, but that there are unquestionably those series in which the boiling-point difference for the elementary difference of $C_2 H_2$ may be greater than 19°, of which Kopp has already furnished some examples.

That the difference may also be *less* than 19° in some series receives confirmation from the facts presented in the following tables.

6. *Of the Nitro-compounds derived from the Hydrocarbons of the Benzole Series.*

Name of Substance.	Formula.	Boiling-point.	Elementary Difference.	Difference of Boiling-point.
Nitro-benzole,	$C_{12} H_5 NO_4$	212°.1		
Nitro-toluole,	$C_{14} H_7 NO_4$	225.9	$C_2 H_2$	13°.8
Nitro-xylole,	$C_{16} H_9 NO_4$	239.3	$C_2 H_2$	13.4
Nitro-isocumole,	$C_{18} H_{11} NO_4$		$C_2 H_2$	

7. *Of the Alkaloids derived from the Hydrocarbons of the Benzole Series.*

Name of Substance.	Formula.	Boiling-point.	Elementary Difference.	Difference of Boiling-point.
Aniline,	$C_{12} H_7 N$	184°.6		
Toluidine,	$C_{14} H_9 N$	201.7	$C_2 H_2$	17°.1
Xylidine,	$C_{16} H_{11} N$	216.0*	$C_2 H_2$	
Iso-cumidine,	$C_{18} H_{13} N$		$C_2 H_2$	

In regard to the results presented in the last two tables, it may be remarked, first, that of the difference shown in the table of nitro-compounds, viz. an average of 13°.6, the discrepancy between this and the number 19°, being 5°.6, is so large as to leave no room for reasonable doubt that this is one of those exceptional series in which the boiling-point difference is less than 19° for the elementary difference of $C_2 H_2$. As this series does not appear to have been examined by Kopp, I have taken care to make as accurate a determination of the difference as circumstances would allow. The boiling-points were corrected as usual for pressure and the upper mercurial column. The boiling-points which have already been published of these bodies, so far as I have noticed, appear to have been given in the observed, i. e. uncorrected temperatures. The quantities of nitro-benzole and nitro-toluole which I operated upon were sufficiently large, and of a high degree of purity, presenting perfectly constant boiling-points. The quantity of nitro-xylole, however, was not so large as would have been desirable. Although the boiling-point of this body is doubtless very nearly correct, those of nitro-benzole and nitro-toluole are more to be relied upon; and omitting the fraction, the number 14° may, I think, be safely taken as the true boiling-point difference in this series. Secondly, that the less striking difference presented in the series of alkaloids, being only 2° under the number 19°, cannot reasonably justify the assumption that this small discrepancy of 2° is attributable to impurity of the substances, or to inaccuracy in the determination of the boiling-points, when it is considered that great care was taken to obtain a high degree of purity and accuracy, and when it is considered also that previous observers have made this discrepancy larger than mine. It was on account of the fact that so small a discrepancy would naturally raise a doubt as to the reliability of the determinations, and for the reason that Kopp* has considered this series of alkaloids as agreeing tolerably well with his general law, that special care was taken on my part to arrive at a correct result. I am confident, therefore, that the boiling-point difference here will not be found to vary more than a fraction from 17°. Of the absolute accuracy of the boiling-points themselves I do not speak so confidently, since these depend so much on the accuracy of the thermometer at these high temperatures; but the correction of any errors which may have arisen from this source would not be likely to alter the relation, and the difference between the boiling-points would still remain about the same. This remark applies with equal force as to the reliability of the other boiling-points presented in this paper, especially of those of high temperatures.

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* Not corrected.

It remains now to consider the foregoing facts with reference to the other theories mentioned.

OF THE CALCULATED BOILING-POINTS OF HYDROCARBONS BY SCHRÖDER'S THEORY.

The subjoined tables exhibit the theoretical boiling-points of the above-mentioned hydrocarbons,† as calculated according to Schröder's last theory, in comparison with the boiling-points actually found. By this theory, as already stated, each double atom of carbon (C_2) contained in a body is supposed to influence the boiling-point by 30°, and each double atom of hydrogen (H_2) to influence the same — 10°; from the sum of these influences the number 70° is in all cases to be deducted, in order to find the boiling-point.

1. *Hydrocarbons from Pennsylvania Petroleum.*

1st Series.

Formula.	Determined Boiling-point.	Calculated Boiling-point by Schröder's theory.	Difference between Calculated and Determined Boiling-point.
	°	°	°
$C_8 H_{10}$	0.0 (?)	0	
$C_{10} H_{12}$	30.2	20	10.2
$C_{12} H_{14}$	61.3	40	21.3
$C_{14} H_{16}$	90.4	60	30.4
$C_{16} H_{18}$	119.5	80	39.5
$C_{18} H_{20}$	150.8	100	50.8

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* Annalen der Chemie und Pharmacie, 1855, XCVI. 24.

† To avoid useless repetition, the hydrocarbons from Albert coal-oil will be omitted in this series of tables, they being considered identical with the corresponding bodies from petroleum.

2D SERIES.*

Formula. (?)	Determined Boiling-point.	Calculated Boiling-point by Schröder's theory.	Difference between Calculated and Determined Boiling-point.
$C_8 H_{10}$	8 – 9°	0°	8 – 9°
$C_{10} H_{12}$	37.0	20	17.0
$C_{12} H_{14}$	68.5	40	28.5
$C_{14} H_{16}$	98.1	60	38.1
$C_{16} H_{18}$	127.6	80	47.6

3D SERIES. (*Not completed.*)

Formula.	Determined Boiling-point	Calculated Boiling-point by Schröder's theory.	Difference between Calculated and Determined Boiling-point.
$C_{20} H_{20}$	174°.9	130°	44°.9
$C_{22} H_{22}$	195.8	150	45.8
$C_{24} H_{24}$	216.2	170	46.2

2. *Hydrocarbons from Coal-tar Naphtha.*

Name of Substance.	Formula.	Determined Boiling-point.	Calculated Boiling-point by Schröder's theory.	Difference between Calculated and Determined Boiling-point.
Benzole,	$C_{12} H_6$	80°.0	80°	0°.0
Toluole,	$C_{14} H_8$	110.3	100	10.3
Xylole,	$C_{16} H_{10}$	139.8	120	19.8
Isocumole,	$C_{18} H_{12}$	169.9	140	29.8

3. *The Homologous Hydrocarbons from Oil of Cumin and Cuminic Acid.*

Name of Substance.	Formula.	Determined Boiling-point.	Calculated Boiling-point by Schröder's theory.	Difference between Calculated and Determined Boiling-point.
Cumole,	$C_{18} H_{12}$	151°.1	140°	11°.1
Cymole,	$C_{20} H_{14}$	179.6	160	19.6

It appears, therefore, that the theory of Schröder finds no support from any one of the different series of hydrocarbons presented in these tables. The discrepancy between the observed and calculated boiling-points, as shown, varies from about 10° to 50° C. This discrepancy is found to increase pretty uniformly by about 10° as we rise from one member to the next higher in the ascending series. In the series of the formula $C_n H_n$, however, the discrepancy is nearly a constant one, viz. about 46°. I would not overlook the fact, that the calculated boiling-point of benzole is absolutely identical with that found by experiment; nor the remarkable coincidence, that the agreement is almost perfect between the probable boiling-point, and that obtained by calculation for the body of the probable formula $C_8 H_{10}$ in the 1st Series from petroleum. It is obvious, however, that these are merely accidental circumstances, to which no importance can attach.

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* See foot-note on page 167.

OF THE CALCULATED BOILING-POINTS OF HYDROCARBONS BY LÖWIG'S THEORY, VIZ. THAT ONE ATOM OF CARBON (C) RAISES THE BOILING-POINT 38°.4, AND ONE ATOM OF HYDROGEN (H) LOWERS IT 29°.2.

Hydrocarbons from Pennsylvania Petroleum.

1ST SERIES.

Formula.	Determined Boiling-point.	Calculated Boiling-point by Löwig's theory.	Difference between Calculated and Determined Boiling-point.
$C_8 H_{10}$	0°.0 (?)	15°.2	°
$C_{10} H_{12}$	30.2	33.6	3.4
$C_{12} H_{14}$	61.3	52.0	9.3
$C_{14} H_{16}$	90.4	70.4	20.0
$C_{16} H_{18}$	119.5	88.8	30.7
$C_{18} H_{20}$	150.8	107.2	43.6

2D SERIES.*

Formula. (?)	Determined Boiling-point.	Calculated Boiling-point by Löwig's theory.	Difference between Calculated and Determined Boiling-point.
$C_8 H_{10}$	8°–9	15°.2	6°.7
$C_{10} H_{12}$	37.0	33.6	3.4
$C_{12} H_{14}$	68.5	52.0	16.5
$C_{14} H_{16}$	98.1	70.4	27.7
$C_{16} H_{18}$	127.6	88.8	38.8

3D SERIES. (*Not yet completed.*)

Formula.	Determined Boiling-point.	Calculated Boiling-point by Löwig's theory.	Difference between Calculated and Determined Boiling-point.
$C_{20} H_{20}$	174°.9	184°.0	10°.9
$C_{22} H_{22}$	195.8	202.4	6.6
$C_{24} H_{24}$	216.2	220.8	4.6

A cursory examination of the last three tables will suffice to show that, so far as regards the hydrocarbons of the formulæ $C_n H_n$ and $C_n H_{n+2}$, the theory of Löwig also has no foundation in fact. That his theory did not hold good with the hydrocarbons of the formula $C_n H_{n-6}$ was observed by Löwig himself, who found that it would place the boiling-point of benzole at 285°.6, i. e. 205° above its actual boiling-point.

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* See foot-note on page 167.

Of the Calculated Boiling-points of Hydrocarbons by Gerhardt's Theory.

We come finally to test the law of Gerhardt, above mentioned. Inasmuch as this law was specially designed to apply exclusively to the hydrocarbons, — upon the observed boiling-points of some of which it was indeed founded, — we should naturally expect to find this more in accordance with facts than either the hypothesis of Schröder or that of Löwig, both of which were claimed to be of more general application, and were framed more especially with reference to other classes of substances. The facts presented in the following tables will show, however, that this is far from being the case; and that the theory of Gerhardt, as well as those of Schröder and Löwig, so far as these relate to the hydrocarbons, was by no means legitimately drawn from nature, but is altogether artificial.

1. *Hydrocarbons from Pennsylvania Petroleum.*

1st Series.

Formula.	Determined Boiling-point.	Calculated Boiling-point by Gerhardt's theory.	Difference between Calculated and Determined Boiling-point.
$C_8 H_{10}$	0°.0 (?)	—8°.0	°
$C_{10} H_{12}$	30.2	12.5	17.5
$C_{12} H_{14}$	61.3	33.0	28.3
$C_{14} H_{16}$	90.4	53.5	36.9
$C_{16} H_{18}$	119.5	74.0	45.5
$C_{18} H_{20}$	150.8	94.5	56.3

2d Series.*

Formula. (?)	Determined Boiling-point.	Calculated Boiling-point by Gerhardt's theory.	Difference between Calculated and Determined Boiling-point.
$C_8 H_{10}$	8 – 9°	—8°	16°.5
$C_{10} H_{12}$	37.0	12.5	24.5
$C_{12} H_{14}$	68.5	33.0	35.5
$C_{14} H_{16}$	98.1	53.5	44.6
$C_{16} H_{18}$	127.6	74.0	53.6

3d Series.

Formula.	Determined Boiling-point.	Calculated Boiling-point by Gerhardt's theory.	Difference between Calculated and Determined Boiling-point
$C_{20} H_{20}$	174°.9	130°.0	44°.9
$C_{22} H_{22}$	195.8	150.5	45.3
$C_{24} H_{24}$	216.2	171.0	45.2

* See foot-note on page 167.

2. *Hydrocarbons from Coal-tar Naphtha.*

Benzole Series.

Name of Substance.	Formula.	Determined Boiling-point.	Calculated Boiling-point by Gerhardt's theory.	Difference between Observed and Calculated Boiling-point.
Benzole,	$C_{12} H_6$	80°.0	93°.0	13°.0
Toluole,	$C_{14} H_8$	110.3	113.5	3.5
Xylole,	$C_{16} H_{10}$	139.8	134.0	6.0
Isocumole,	$C_{18} H_{12}$	169.9	154.5	15.5

3. *Hydrocarbons from Oil of Cumin and Cuminic Acid.*

Name of Substance.	Formula.	Determined Boiling-point.	Calculated Boiling-point by Gerhardt's theory.	Difference between Observed and Calculated Boiling-point.
Cumole,	$C_{18} H_{12}$	151°.1	154°.5	+3°.4
Cymole,	$C_{20} H_{14}$	179.6	175.0	—4.6
Cumo-oil of turpentine,	$C_{20} H_{16}$	155.4	160.0	+4.6

The chief conclusions deduced from the foregoing facts and considerations may be briefly summed up as follows: —

1. That the boiling-point difference for the addition of $C_2 H_2$ in homologous series of hydrocarbons is generally 30° C., which is a much larger difference than has been commonly supposed.

2. That of the five series of hydrocarbons examined, only one series was found exceptional to the rule just stated, and this presented the boiling-point difference of about 20°, which is but little larger than the number 19°, which Kopp found so common with other classes of substances.

3. That certain series of derivatives from the benzole series of hydrocarbons present boiling-point differences, corresponding to the elementary difference of $C_2 H_2$, considerably smaller than the number 19° of Kopp.

4. That the formulæ of Schröder, Löwig, and Gerhardt for the calculation of boiling-points, so far as these may be supposed to relate to the hydrocarbons, are incorrect and purely artificial.

5. That the custom of taking boiling-points with the bulb of the thermometer in the vapor is more liable to lead to an erroneous determination, at least in certain cases, than if the bulb be placed in the liquid.